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Effect of Preliminary Nanostructuring Frictional Treatment on the Efficiency of Nitriding of Metastable Austenitic Steel in Electron Beam Plasma

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Abstract. The paper studies the effect of the temperature of nitriding in electron beam plasma, ranging between 250 and 500 °C, on the nitrogen concentration, phase composition and microhardness of the surface of the AISI 321 chromium-nickel austenitic steel in two initial states – quenched undeformed and after nanostructuring frictional treatment. The lowest nitriding temperature (350 °C) for the efficient hardening of the steel has been established. The application of frictional pretreatment with a sliding synthetic diamond indenter in an argon environment is shown to be highly efficient for increasing the depth of the layer nitrided at this temperature. The contribution of the formed S-phase (nitrogen-oversaturated austenite γ_N) to the intensive hardening of the steel nitrided at low temperatures (300 to 400 °C) is noted.

INTRODUCTION

Nitriding in low-energy electron beam plasma is a state-of-the-art method for thermochemical modifying of non-heat-treatable austenitic chromium-nickel steels [1, 2]. Of special interest is plasma nitriding at a temperature below 450 °C, which results in the formation of the metastable γ-phase of an oversaturated solid solution of nitrogen exhibiting high hardness (12 to 15 GPa) and corrosion resistance. At higher temperatures, in the near-surface layer of the steel the CrN nitride phase is formed. This reduces the chromium atoms flux to the surface and leads to the loss of the ability to form a protective oxide layer and a decrease in the corrosion resistance of the steel [3]. Therefore, it is urgent to find ways of increasing the rate of nitrogen diffusion into the bulk of the material to be modified at low nitriding temperatures. The efficiency of the process of low-temperature plasma nitriding can be enhanced by preliminary deformation nanostructuring deformation treatments, particularly, by SMAT (surface mechanical attrition treatment) [4, 5]. Treatments with sliding indenters are practically relevant surface treatment methods [6, 7]. Nanostructuring and intensive strain hardening of the surface layer of an austenitic chromium-nickel steel with the simultaneous formation of low surface roughness is achieved by frictional treatment with a synthetic diamond indenter in an argon environment [8, 9]. The aim of the paper is to study the hardening, nitrogen saturation and phase composition of the surface of the AISI 321 austenitic steel after combined treatment including nanostructuring frictional treatment and nitriding in electron beam plasma at temperatures ranging between 250 and 500 °C and, for comparison, after nitriding of an undeformed nacrocrystalline steel.

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EXPERIMENTAL PROCEDURE

The AISI 321 corrosion-resistant austenitic steel of the following composition was studied (wt%): 0.04C, 16.77Cr, 8.44Ni, 1.15Mn, 0.67Si, 0.32Ti, 0.31Cu, 0.26Mo, 0.12Co, 0.12V, 0.04P, 0.03Nb, 0.005S, and the rest Fe. Specimens sized 40×20×10 mm were cut out from sheet steel by spark cutting and quenched from 1100 °C with water cooling, mechanically ground, electrically polished and treated by friction. Frictional treatment was performed with a sliding synthetic diamond indenter with the hemisphere radius R=3 mm in a nonoxidizing argon environment, with the load on the indenter P=294 N, with a single indenter scan, with a 0.02-mm displacement after each double stroke of the reciprocating indenter. Then, the specimens were chemically purified in an ultrasonic bath of acetone for 10 minutes and placed into a vacuum chamber for subsequent ion-plasma treatment. A source of electrons with a plasma cathode based on a glow discharge with a cold hollow cathode, a widened anode part and a single-net wide beam forming system [1] was used to generate plasma in the volume of the vacuum chamber. Bias voltage of −120 V, negative with respect to plasma, was applied to the specimens. The temperature of the nitrided specimens (from 250 to 500 °C) was controlled by the variation of the beam current (1.2 to 7.0 A), electron energy (120 to 200 eV) and the density of the current of ions (1.0 to 7.5 mA/cm^2) arriving at the specimen surface.

The microhardness was determined on a Shimadzu HMV-G21DT microhardness tester under loads ranging between 0.25 and 4.90 N on the Vickers indenter. Nitrogen concentration on the surface was determined by the nuclear reaction method on a Van de Graaff accelerator. The depth of the analyzed layer amounted to 2.5 μm. The phase composition of the coatings was examined on a Shimadzu XRD-7000 X-ray diffractometer in Crk$_\alpha$-radiation.

RESULTS AND DISCUSSION

Figures 1 and 2 characterize nitrogen concentrations, determined by the nuclear reaction method, in the surface layer of the AISI 321 steel specimens, in the initial macrocrystalline quenched state (electropolishing) and after nanostructuring by frictional treatment, nitrided in electron beam plasma at different temperatures T_N. Figure 1 exemplifies nitrogen distribution through the depth of the surface layer of the specimens nitrided at T_N=400 °C. It follows from fig. 2 that the initial macrocrystalline electropolished steel has maximum nitrogen concentrations (43 to 44 at.%) directly on the surface after nitriding at T_N=350−450 °C (curve 1*a*), and in the layer at a depth of 0.50 to 2.25 μm the nitrogen content of about 30 at.% is observed for the specimens nitrided at 350−450 °C (curve 1*b*). Lower nitrogen concentrations (23 at.%) in the electropolished specimen after nitriding at T_N=500 °C results from a higher rate of nitrogen diffusion at this temperature and nitrogen penetration from the surface into deeper layers.

The steel with the surface layer nanostructured by frictional treatment, after nitriding at T_N=350–450 °C, has lower carbon concentrations directly on the nitrided surface (curve 2*a* in fig. 2) as compared to the nitrided macrocrystalline state (curve 1*a*). In the layer at a depth of 0.50 to 2.25 μm, the deformed specimens have lower nitrogen concentrations (curve 2*b*) than the undeformed ones (curve 1*b*) only at the nitriding temperature T_N=350 °C.

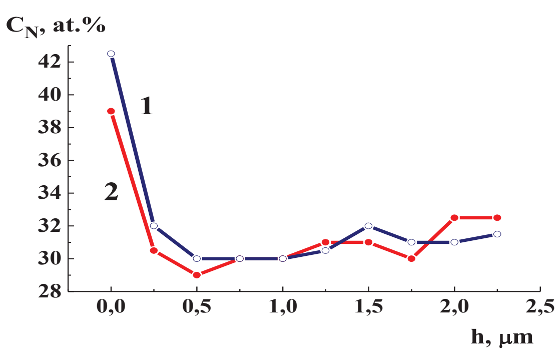


FIGURE 1. Nitrogen concentration distribution C_N through the depth *h* of the surface layer of AISI 321 steel specimens: 1 – electropolishing + nitriding at T_N=400 °C; 2 – frictional treatment + nitriding at T_N=400 °C

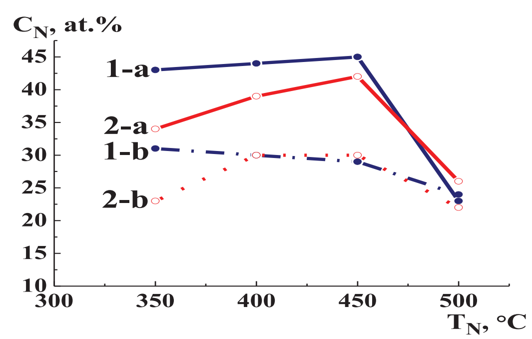
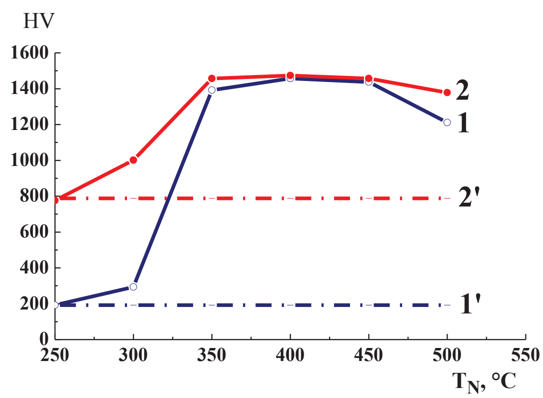


FIGURE 2. Effect of the nitriding temperature T_N on nitrogen concentration C_N on the surface (1*a*, 2*a*) and in the surface layer at a depth of 0.50–2.25 μm (1*b*, 2*b*) in AISI 321 steel specimens: 1*a*, 1*b* – electropolishing + nitriding; 2*a*, 2*b* – frictional treatment + nitriding

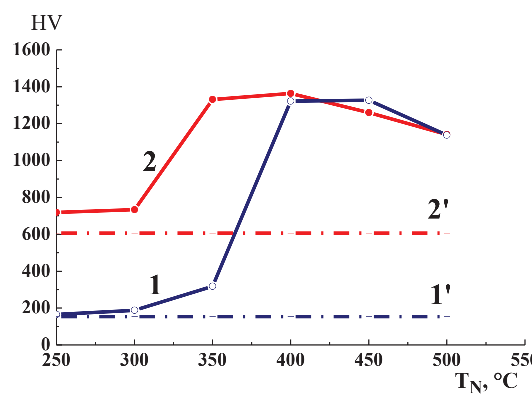
Figure 3 shows the microhardness of the nitrided surface as dependent on the temperature of nitriding. The use of different loads on the Vickers indenter (0.25 N and 2.94 N) for microhardness measurements has enabled us to analyze layers of different thickness due to different depth of indenter penetration into the material. It is obvious that there is not steel hardening at T_N=250 °C. The microhardness measurements under the minimum load of 0.25 N (fig. 3*a*) have shown that at T_N=300 °C there is only a small hardening of the thin surface layer of the steel both in the initial electropolished state and after frictional treatment. At T_N=350–450 °C, maximum hardening of the thin surface layer is achieved, up to 1390−1460 HV0.025. Hence, the temperature of 300 °C is the lower temperature limit of nitriding, the minimum temperature of efficient electron beam plasma nitriding is T_N=350 °C.

As the load on the indenter increases to 2.94 N (accordingly, in the analysis of deeper surface layers), the initial electropolished steel, for the nitriding temperature T_N=400–500 °C, has only a fairly small decrease in microhardness (fig. 3*b*, curve 1) as compared to the measurements under lower loads (fig. 3*a*, curve 1). However, at T_N=350 °C, the microhardness of the nitrided quenched steel decreases sharply from 1400 HV0.025 (under the load on the indenter of 0.25 N) to 320 HV0.3 (under the load on the indenter of 2.94 N) (fig. 3*a*, *b*, curves 1). This points to a significantly smaller thickness of the layer nitrided at T_N=350 °C than that of the layer nitrided at T_N=400–500 °C for the initial macrocrystalline state of the steel.

Frictional treatment provides strain hardening of the AISI 321 steel (fig. 3*a*, *b*, curves 2'). The lower level of hardening determined by measurements with a load on the indenter of 2.94 N (590 HV0.3) than that with the load of 0.25 N (790 HV0.025) stems from a sharp gradient of decreasing microhardness through the depth of the surface layer of austenitic steel hardened by frictional treatment [8]. As distinct from the nitriding of the initial macrocrystalline steel (curves 1), in the case that the steel subjected to frictional treatment is nitrided, the decrease of nitriding temperature from 400 to 350 °C does not cause any notable decrease in microhardness as the load on the indenter increases to 2.94 N (fig. 3*a*, *b*, curves 2). Consequently, the preliminary nanostructuring of the surface layer of the steel by frictional treatment increases significantly the depth of the layer efficiently hardened by nitriding at T_N=350 °C. It is nitrogen penetration from the surface into deeper layers that seems to have caused lower nitrogen concentrations after nitriding at T_N=350 °C observed in fig. 2 for the steel subjected to frictional treatment, than those observed for the undeformed steel.



(a)



(b)

FIGURE 3. Effect of nitriding temperature T_N on the microhardness HV of the surface of the AISI 321 steel specimens with the loads on the Vickers indenter of 0.25 N (*a*) and 2.94 N (*b*): 1 – electropolishing + nitriding (1' – electropolishing); 2 – frictional treatment + nitriding (2' – frictional treatment)

This principal result is supported by the data presented in fig. 4 on the behavior of the microhardness of the steel nitrided at T_N=350 °C with the load on the Vickers indenter increasing from 0.25 to 4.90 N. Indeed, for the nitrided steel in the initial undeformed state, the increasing load on the indenter significantly decreases the microhardness to as low as 260 HV0.5, with the load on the indenter of 4.90 N, (fig. 4, curve I). This testifies to a small thickness of the nitrided layer in the undeformed steel. The microhardness of the steel subjected to frictional treatment and nitrided at T_N=350 °C, as the load on the indenter increases to 4.90 N, decreases much less intensively, and it does not decrease below 1190 HV0.5 (fig. 4, curve II). The discussed results of the microdurometric study are indicative of a significantly deeper nitrided layer in the case that the austenitic steel undergoes a combined treatment including nanostructuring frictional treatment before nitriding. X-ray diffraction analysis has revealed that, after nitriding at T_N=500 and 450 °C, the main phases on the steel surface are the ε-phase ($Fe_{2-3}N$) and the γ′-phase (Fe_4N).

Chromium nitride CrN is formed at T_N=500 °C on the surface of electropolished and frictionally treated steel, and at T_N=450 °C it is formed only after preliminary nanostructuring treatment. As the nitriding temperature decreases to T_N=400, 350 and 300 °C, besides the ε- and γ′-phases, in the structure there appears the S-phase, i. e. nitrogen-oversaturated austenite γ_N. The formation of these phases is responsible for the hardening of the surface of the austenitic steel when it is nitrided in electron beam plasma. Besides, the structure of the AISI 321 steel subjected to frictional treatment and nitriding at T_N=350 and 300 °C is characterized by the presence of the α′-phase, i. e. strain-induced martensite, whose quantity on the surface of this metastable steel after frictional treatment reaches 95 vol.%.

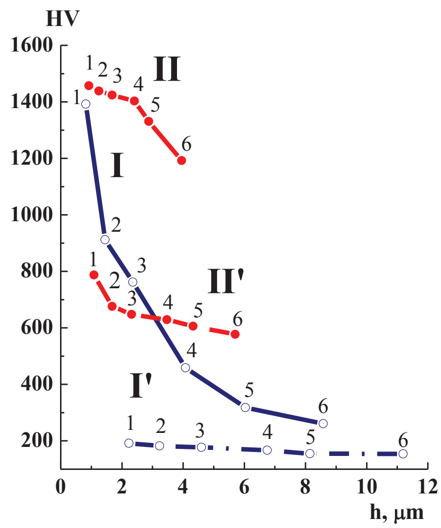


FIGURE 4. The microhardness HV of the AISI 321 steel surface as dependent on the Vickers indenter penetration depth under loads of 0.25 N (1), 0.49 N (2), 0.98 N (3), 1.96 N (4), 2.94 N (5) and 4.90 N (6): I – electropolishing + nitriding at T_N=350 °C (I' – electropolishing); II – frictional treatment + nitriding at T_N=350 °C (II' – frictional treatment)

CONCLUSIONS

It has been established that the preliminary nanostructuring of the surface layer of the AISI 321 austenitic chromium-nickel steel by frictional treatment with an synthetic diamond indenter in an argon environment causes a significant increase in the thickness of the layer hardened by subsequent nitriding in electron beam plasma at the nitriding temperature T_N=350 °C. As the nitriding temperature decreases to T_N=300 °C, the efficiency of hardening sharply decreases, and there is no steel hardening after nitriding at T_N=250 °C. By the nuclear reaction method, after electron beam plasma nitriding of a quenched undeformed steel at temperatures ranging between 350 and 450 °C, maximum nitrogen concentrations have been determined on the surface (up to 44 at.%) and in the layer at a depth of 0.5 to 2.25 μm (up to 30 at.%). The discovered lower nitrogen concentrations in prestrained specimens may be due to nitrogen reflux into the deeper layers of the nanostructured steel. Efficient surface hardening during nitriding (up to 1460 HV0.025) is due to the formation of the S-phase (nitrogen-oversaturated austenite γ_N) at T_N=350–400 °C, the ε-phase $Fe_{2-3}N$ and the γ′-phase Fe_4N, as well as chromium nitride CrN forming on the surface of the quenched steel only at T_N=500 °C and in the surface layer of the nanostructured steel at T_N=450–500 °C.

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